Linking polymer properties to process conditions for vinyl chloride suspension polymerization processes

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Producers of polymers in general and of poly(vinyl chloride) in particular strive for certain customer specified properties that are controlled by fundamental polymer properties, such as the molar mass distribution (MMD) and the content of structural defects (branches and unsaturations). The latter influences to a large extent the thermal stability of the polymer product. Considering the industrial importance of the vinyl chloride suspension polymerization process, it is critical to develop models linking polymer properties to the applied process conditions.

In this contribution a fundamental kinetic model describing the vinyl chloride free radical polymerization at the elementary reaction level while systematically accounting for diffusion limitations, is presented. By considering all involved elementary reactions and structurally different radical species, the structural defects content can be determined. The method of moments is applied to calculate the averages of the MMD.

Possible diffusion limitations are accounted for by calculating apparent rate coefficients for all elementary reactions, consisting of an intrinsic and a diffusion contribution. The former is obtained via regression of experimental data or from literature, whereas the latter is systematically calculated using the Smoluchowski expression in which the diffusion coefficients are determined using the free volume theory [1].

The combination of the resulting kinetic model with an appropriate reactor model enables the calculation of the monomer conversion, the averages of the MMD and the structural defects content as a function of polymerization time for a wide range of process conditions [2]. Validation of the presented model is performed by comparing both laboratory scale and pilot scale model calculations and experimental data. Based on the good agreement of model calculations and experimental data it can be concluded that the proposed model is applicable in design, optimization and control of industrial poly(vinyl chloride) suspension polymerization reactors [3]. Furthermore it could be concluded from model calculations that structural defects are predominantly formed at high monomer conversions when monomolecular reactions are favoured over bimolecular reactions.

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